COATINGS. ENAMELS

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EFFECT OF ALKALINE-EARTH METAL OXIDES ON THE PROPERTIES OF BORON-FREE TITANIUM ENAMELS

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The studies showed that alkaline-earth metal oxides affect the properties of boron-free enamels differently, in particular, magnesium oxide increases the whiteness of the coatings, and strontium oxide improves their luster only when less than 1% is added, while calcium oxide negatively affects both the whiteness and the luster of the coatings in the amounts investigated. It should be noted that the effect of these alkaline-earth oxides on the properties of boron-free enamels is similar to their effect on the properties of boron-containing enamels.

Key words: alkaline-earth metal oxides, frits, boron-free enamel coatings, whiteness.

In the synthesis and investigation of titanium borosilicate glasses and enamels, the important effect of alkaline-earth metal oxides on their physicochemical properties and especially on crystallization of the glasses and coatings was found. It was noted in [1] that divalent metal oxides can be placed in the following order based on the effect on devitrification of these enamels: BaO < SrO < CaO < CdO < MgO < ZnO < BeO.

There are also published data [2] that indicate that magnesium oxide in titanium borosilicate enamels causes separation of smaller anatase crystals, producing soft white coatings, and limits formation of rutile, which gives the opacified glass coating a yellowish hue. At the same time, it is necessary to note that there are no published data on the effect of alkaline-earth metal oxides on the physicochemical properties of boron-free titanium-containing enamels, especially the whiteness and luster of the coatings made from them. This stimulated interesting in studying the effect of MgO, CaO, and SrO on the properties of synthesized boron-free enamel coatings. These metal oxides form the second group in the periodic table were selected because they are nontoxic, in contrast to the others, and can be used to fabricate items for household use.

The effect of the alkaline-earth metal oxides was investigated in enamel composition No. 18-7 in the $Na_2O – Al_2O_3 – P_2O_5 – TiO_2 – SiO_2 – Na_3AlF_6$ system [3]; these divalent oxides (MgO, CaO, and SrO) were added instead of Na_2O in the amount of 1, 2, and 3%[3] both individually and in different ratios [4]. This substitution was to reduce the effect of the alkaline oxides on the solubility of TiO_2 in the melt and to improve the opacification of the coatings. disposition of the experimental compositions (see Table 1) is presented in the design of the experiment (Fig. 1).

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[3] Here and below — content by weight.

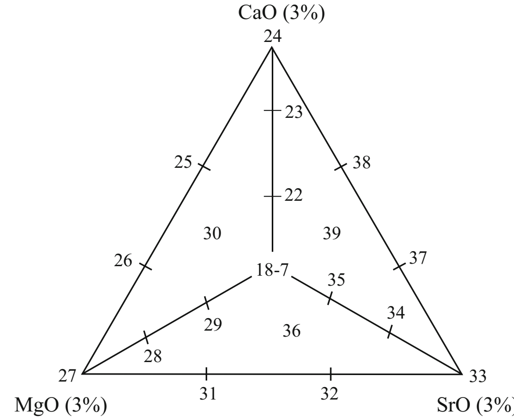

Fig. 1. Position of experimental enamel compositions in the experimental design in substitution of Na_2O by CaO, MgO, and SrO (the composition numbers are according to Table 1).

TABLE 1. Physicochemical Properties of Enamel Frits and Coatings Made from Them

Enamel composition	Mass content, %			Water resistance, cm^3/g	$t_{i.s}$, °C	CLTE, 10^{-7} K^{-1}	Whiteness, %	Luster, %
	CaO	MgO	SrO					
18-7	–	–	–	0.115	575	89	68.60	90
22	1	–	–	0.113	560	89	68.63	28
23	2	–	–	0.083	551	90	64.53	9
24	3	–	–	0.070	554	91	69.64	35
25	2	1	–	0.076	573	84	79.05	50
26	1	2	–	0.065	580	87	82.84	71
27	–	3	–	0.062	591	86	82.35	45
28	–	2	–	0.055	586	87	81.80	75
29	–	1	–	0.092	575	89	74.35	57
30	1	1	–	0.078	580	85	72.70	49
31	–	2	1	0.063	570	87	81.27	71
32	–	1	2	0.078	573	82	74.46	30
33	–	–	3	0.068	580	82	65.11	22
34	–	–	2	0.092	575	85	63.63	50
35	–	–	1	0.110	553	90	64.64	88
36	–	1	1	0.108	567	85	70.84	54
37	1	–	2	0.093	568	83	64.28	23
38	2	–	1	0.100	560	88	68.47	69
39	1	–	1	0.088	556	87	64.30	30

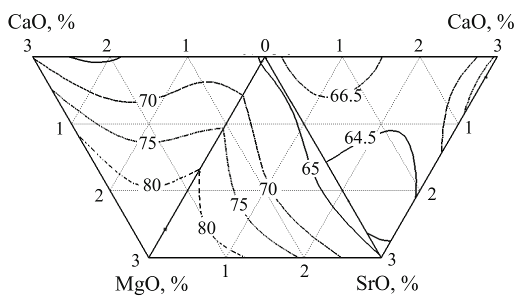

Fig. 2. Effect of substitution of Na_2O by CaO, MgO, and Sr O on the whiteness of the investigated enamels, %.

The physicochemical and optical properties of the frits and coatings made from them are presented in Figs. 2 – 4 and in Table 1.

The analysis of the quality and properties of the boron-free titanium enamel coatings fired at temperatures of 750 – 870°C showed that substitution of Na_2O by CaO and SrO in the concentrations investigated almost did not change the whiteness of the enamel coatings — the diffuse reflection coefficient (DRC) was within 63.6 – 69.6%; however, their luster dropped sharply: the mirror-reflection coefficient (MRC) decreased from 96 to 9% (2% CaO) and 22 (3% SrO). The latter is due to the coarse crystallization of the enamel layer even for a low (under 1%) CaO content.

Magnesium oxide in the amount of up to 3% increases the whiteness of the boron-free enamel glass layer from

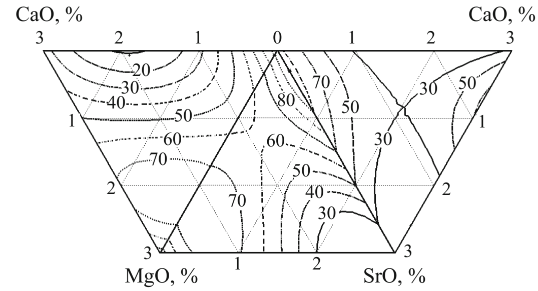

Fig. 3. Effect of substitution of Na_2O by CaO, MgO, and SrO on the luster of the enamel coatings, %.

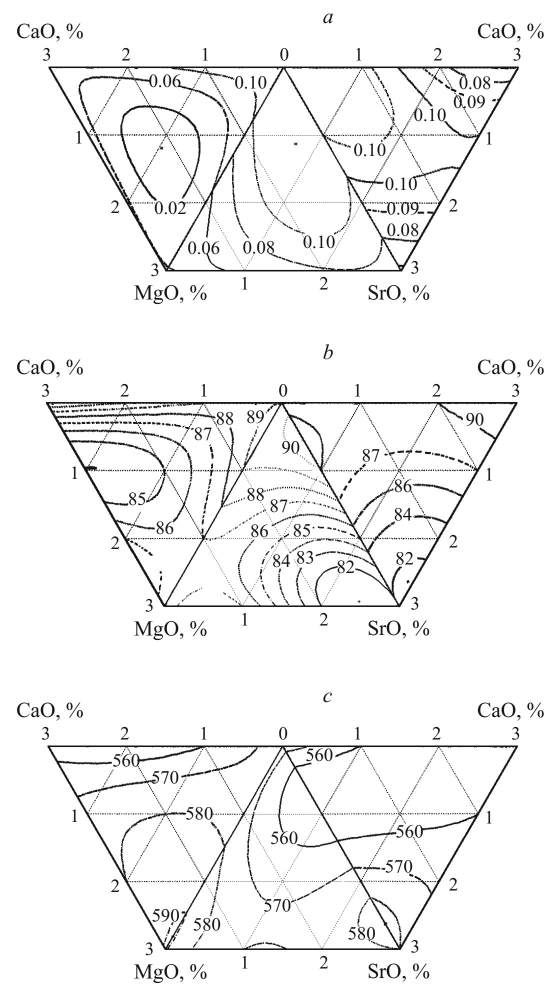

Fig. 4. Leachability (*a*), TCLE (*b*), and initial softening point $t_{i.s}$ (*c*) of enamel glasses as a function of the content of MgO, CaO, and SrO added instead of sodium oxide.

63.84 to 82.35%, in contrast to calcium and strontium oxides. This is due to both the decrease in the amount of alkaline oxides and the decrease in the degree of reduction of TiO_2, which is in agreement with the published data [5] and is confirmed by the crystallizability of the frits (Fig. 5), as well as the x-ray phase analysis of the enamel coatings (Fig. 6). When the concentration of MgO changed, the composition of

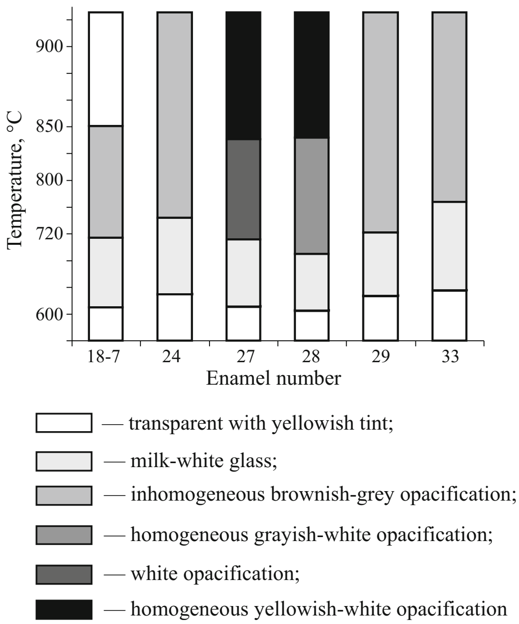

Fig. 5. Crystallizability of glasses containing alkaline-earth metal oxides.

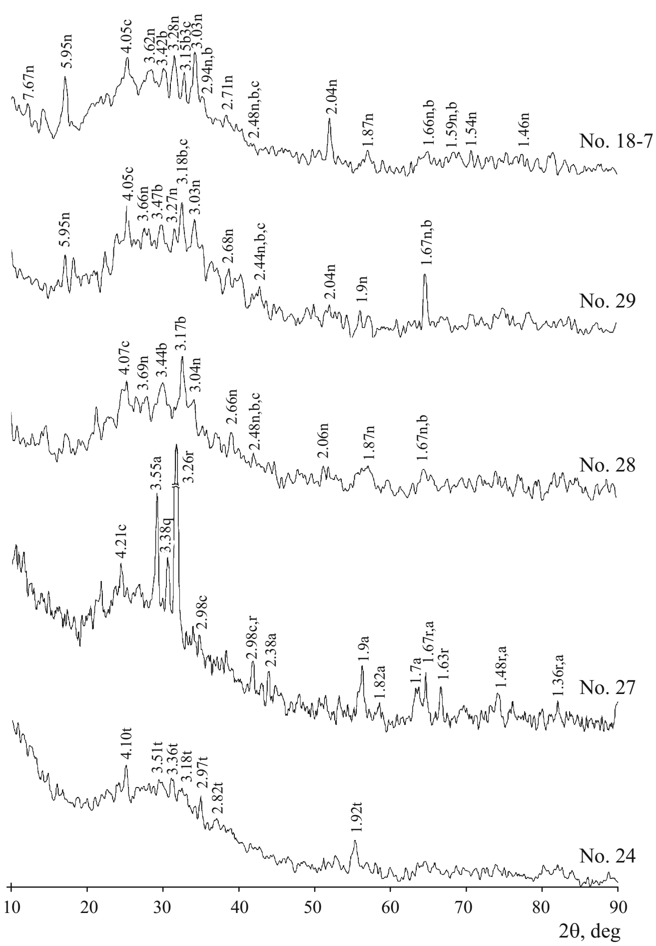

Fig. 6. X-ray patterns of experimental enamels: r) rutile (TiO_2), b) brookite (TiO_2), n) $Na_2O \cdot 6TiO_2$, c) β-crystobalite, a) anatase (TiO_2), q) quartz; t) $Ti_2O_3 \cdot 3TiO_2$.

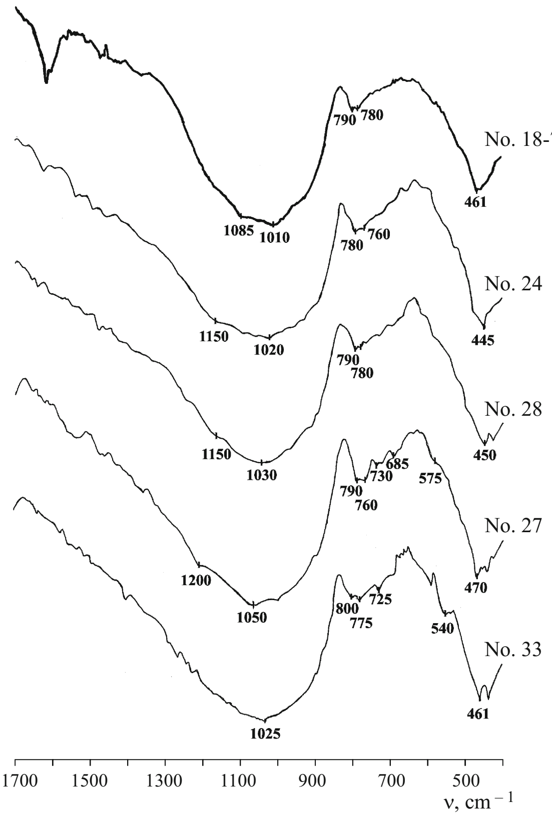

Fig. 7. Infrared absorption spectra of glasses.

the crystalline phases that ensure the opacification of the glass layer: the amount of alkaline titanate decreased and the amount of brookite (for a 1 – 2% MgO content) and anatase and rutile (for a 3% MgO content), increases.

When calcium oxide is added to the enamel, even in the amount of 3%, the compound $Ti_2O_3 - 3TiO_2$, containing titanium ions in the reduced state that give the coating a grayish hue, is the crystalline phase in the coating, and the DRC is low (69%).

In substituting MgO (cation with a smaller radius of 0.074 nm) for Na_2O (cation with a larger radius of 0.098 nm) in these enamels, the leachability decreased from 0.115 to 0.062 cm^3/g as a result of strengthening of the structural network of the glass. This was also confirmed by the data from the spectral studies, that is, by shifting of the basic absorption band to the high-frequency region from 1010 to 1050 cm^{-1} (Fig. 7). The appearance of an absorption band at 685 cm^{-1} is probably due to the appearance of a four-coordination magnesium ion. We know that alkaline-earth metal cations with a small radius (Mg^{2+}) and oxygen cation high bond strength (155 $kJ \cdot mole^{-1}$) strengthen the structure of the glass to a greater degree. With an increase in the radius of the Ca^{2+} (0.106 nm) and Sr^{2+} (0.127 nm) cations, their strengthening effect decreased, and only an insignificant shift in the basic absorption band to the high-frequency region from 1010 to 1020 and 1025 cm^{-1}, respectively, was observed. The water resistance of the experimental frits in-

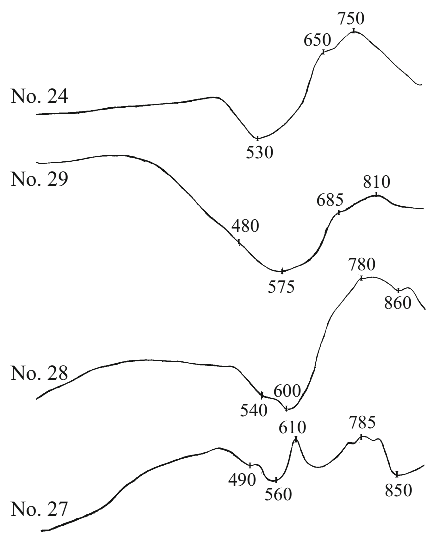

Fig. 8. Differential thermal analysis of glass frits.

creased from 0.115 to 0.07 (3% CaO) and 0.068 cm^3/g (3% SrO).

The data from differential thermal analysis of the experimental glass frits (Fig. 8) also suggest that the size of the crystals formed from the enamel melt (No. 24) containing calcium oxide is larger than on addition of magnesium oxide, as the more gently sloping shape of the curve of the exothermic crystallization effect indicates and which is confirmed by the decrease in the luster of the coatings. The sharp exothermic effect in DTA of the glass (No. 27) at 610°C indicates a rapid crystallization rate with formation of a large number of small crystals, which causes the elevated whiteness of the coatings (82%).

The results of the studies of the effect of alkaline-earth metal oxides on the properties of boron-free enamels are in agreement with the data in [6] for boron-containing enamels: incorporation of cations with a small radius (BeO, ZnO, MgO) causes bulk crystallization in the glasses, and introduction of CaO, SrO, BaO, and CdO results in surface crystallization.

The major possibility of increasing the whiteness of boron-free titanium enamel coatings by partial substitution of sodium oxide by magnesium oxide and production of coatings characterized by a diffuse reflection coefficient of 80 – 82% and luster of up to 75% at a firing temperature of 840°C was thus established. Incorporation of CaO and SrO in the experimental enamels does not produce positive results on the whole, since they do not increase the whiteness of the enamel coatings; CaO decreases the luster of the coatings, worsening their quality, while SrO increases the luster of the glass layer when only up to 1% is added.

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